Title: SULFUR REDUCTION IN GASOLINE AND DIESEL FUELS BY EXTRACTION/ADSORPTION OF REFRACTORY DIBENZOTHIOPHENES

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Abstract

Objective

In order to prevent pollution of the atmosphere by sulfur oxides, it is necessary to remove sulfur from gasoline and diesel fuels. The current EPA-mandated 0.04% limit on sulfur in gasoline will be reduced to 0.0025% by 2006. This reduction will require the development of new technologies that will remove the unreactive dibenzothiophene (DBT) derivatives that contain alkyl groups in the 4,6 positions near the sulfur. These compounds constitute the bulk of the remaining sulfur compounds in hydrotreated petroleum feedstocks.

Accomplishments to Date

1. Extraction of Dibenzothiophenes from Petroleum Feedstocks Using Solutions of Ruthenium Complexes. The known ability of ruthenium (II) complexes to bind dibenzothiophenes in solution is the basis for our process for removing dibenzothiophenes from petroleum feedstocks. Although no fully-characterized metal complexes of 4,6-Me_2DBT have been previously reported, we find that $Ru(NH_3)_5(OH_2)^{2+}$ reacts with 4,6-Me_2DBT to give the $Ru(NH_3)_5$(4,6-Me_2DBT)$^{2+}$ complex.

The $Ru(NH_3)_5(H_2O)^{2+}$ compound also reacts with thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) at room temperature in either acetone or dimethylformamide (DMF). We use this reaction to extract dibenzothiophenes from simulated gasoline (45% toluene, 55% hexanes) containing DBT by mixing this hydrocarbon phase with an aqueous phase (70% DMF, 30% H_2O) that contains $Ru(NH_3)_5(H_2O)^{2+}$. We have found that the $Ru(NH_3)_5(H_2O)^{2+}$, extracts over 50% of the DBT from the simulated petroleum. The DBT is removed from the $Ru(NH_3)_5(DBT)^{2+}$ in the aqueous phase by air oxidation, which generates a ruthenium(III) complex that has a very low affinity for DBT. The ruthenium(III) complex is reduced to reform $Ru(NH_3)_5(H_2O)^{2+}$, thereby completing a cyclic process that removes DBT from petroleum feedstocks and regenerates the $Ru(NH_3)_5(H_2O)^{2+}$ extractant.

2. Removal of Dibenzothiophene from Petroleum Feedstocks Using Solid Adsorbents. In principle, the removal of sulfur compounds from petroleum feedstocks would be more economical if a solid adsorbent were used instead of an extracting solution. We therefore adsorbed $Ru(NH_3)_5(H_2O)^{2+}$ onto solid silica. The attachment of the complex appears to occur through hydrogen bonds as indicated by DRIFT-IR and

MAS ^{29}Si-NMR spectroscopy. The adsorbed complex, when stirred with the simulated petroleum, extracts DBT and 4,6-Me_2DBT.

Plans for the Coming Year

Future work on this project will focus on optimizing the adsorption process by studying other metal complexes and solid substrates.

Articles, Presentations and Supported Students

Journal Articles

McKinley, S.G.; Angelici, R.J. "Extraction of Dibenzothiophenes from Petroleum Feedstocks Using a Ruthenium Complex in Water" *Energy & Fuels*, Submitted for publication.

Presentations

McKinley, S.G. "New Methods for the Removal of Sulfur from Petroleum" Department of Chemistry, Iowa State University, February 27, 2002.

Supported Students

Scott G. McKinley, a Ph.D. graduate student in chemistry
Paul A. Vecchi, a Ph.D. graduate student in chemistry
Dr. Celedonio Alvarez, a postdoctoral associate from Oviedo, Spain